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DEPARTMENT OF COMMERCE
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A CONVENIENT MIXTURE FOR TESTING THE OPERATING EFFICIENCY OF A DISTILLING COLUMN

(A.P.I. Project No.6, Oct. 1, 1930)

1. Introduction

The desirable characteristics of a mixture for testing the operating efficiency of a distilling column are the following:

(1) It should be composed of two stable substances boiling only a few -- not more than say five -- degrees apart.

(2) The constituents should form an ideal solution with each other.

(3) The constituents should be inexpensive and readily obtainable.

(4) A convenient method for the rapid and accurate analysis of the mixture should be available.

A mixture of CCl_4 and C_6H_6 meets all of the above requirements except No.3. Failure to meet this requirement means that fractionation near one end of the composition range is more difficult than near the other, owing to the fact that the pair of boiling point-composition curves is not symmetrical.

A better mixture can be obtained by substituting ethylene chloride, $C_2H_4Cl_2$, in place of CCl_4. This liquid forms an ideal solution with C_6H_6 and also meets all of the other requirements. The boiling point-compositiondiagram is shown in Fig.1.

The mixture can be easily and rapidly analyzed by measuring the refractive index. The density would serve equally well as an index of composition but would require a careful determination of the density-composition relation, which is not known at present.

2. Preparation of the Mixture

A 50-50 mole-percent mixture (1 part C_6H_6 to 1.3683 parts $C_2H_4Cl_2$, weights in air) of the pure dry liquids should be prepared and kept in a bottle containing some "Dehydrite" ($Mg(ClO_4).3H_2O$). This drying agent has a negligible solubility in the mixture. The refractive indices at 35.2°C of each pure liquid and of the mixture should be carefully determined. This temperature is selected because the available refractivity data happen to be for 35.2°C.

3. Using the Mixture

Before filling the still pot with the mixture, the pot, column, condenser and receiver should be clean and dry. Drying is best accomplished with a stream of dry air.

4. Analyzing the Fractions.

The distillation fractions are analyzed by measuring their refractive indices at 25.2°C and computing the composition with the aid of the equations

$$(M\%)_E = (M\%)_{calc.} - \Delta$$

$$(M\%)_{calc.} = \frac{100\ (n_B - n)}{n_B - n_E}$$

$(M\%)_E$ = Mole per cent $C_2H_4Cl_2$

$n_B = n_D^{25.2°}$ for the benzene

$n = n_D^{25.2°}$ for the fraction

$n_E = n_D^{25.2°}$ for the ethylene chloride

Δ is read from the curve in Fig.2.

5. Efficiency Curve

The efficiency graph for a given still and a given mode of operation is obtained by plotting volume of fraction against composition as illustrated in Fig.3 or by making the corresponding differential plot as illustrated in Fig.4.

After completing the test the fractions may be returned to the stock bottle, the contents of which can be kept at the 50-50 composition by "doctoring" occasionally with a little of the required pure component until the original refractive index is restored.

6. Purification of the Constituents

(a) Ethylene Chloride

Ethylene chloride equal in quality to the best grade made by Eastman requires to be distilled only once from a suitable drying agent (Dehydrite) in a good column still with rejection of the initial and final fractions.

Yield, about 85 volume per cent

$n_D^{25.2}$ about 1.4418

(b) Benzene

A good grade of C.P. benzene should be selected and treated as follows:

(1) Wash for 1 hour (preferably in a shaking machine) with 0.1 of its volume of C.P. concentrated H_2SO_4.

(2) Wash successively with water, dilute NaOH and water.

(3) Shake with mercury until tarnishing ceases.

(4) Shake with anhydrous $CaCl_2$ and then with Dehydrite.

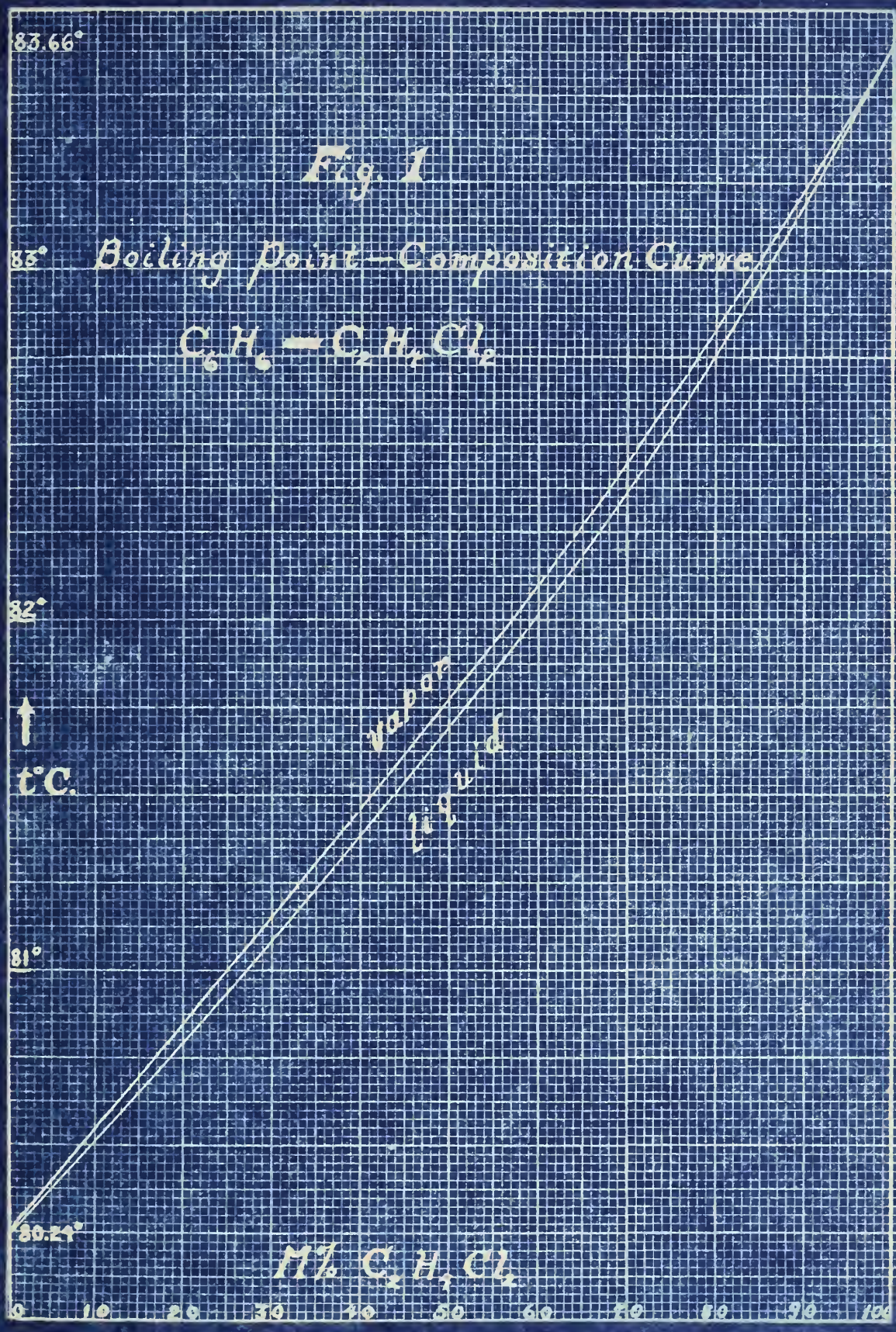
(5) Distil once in a good column still and combine fractions having refractive indices within $\pm 5 \times 10^{-4}$ of the index of the middle fraction.

(6) Crystallize once, rejecting mother liquor about 15 per cent by volume.

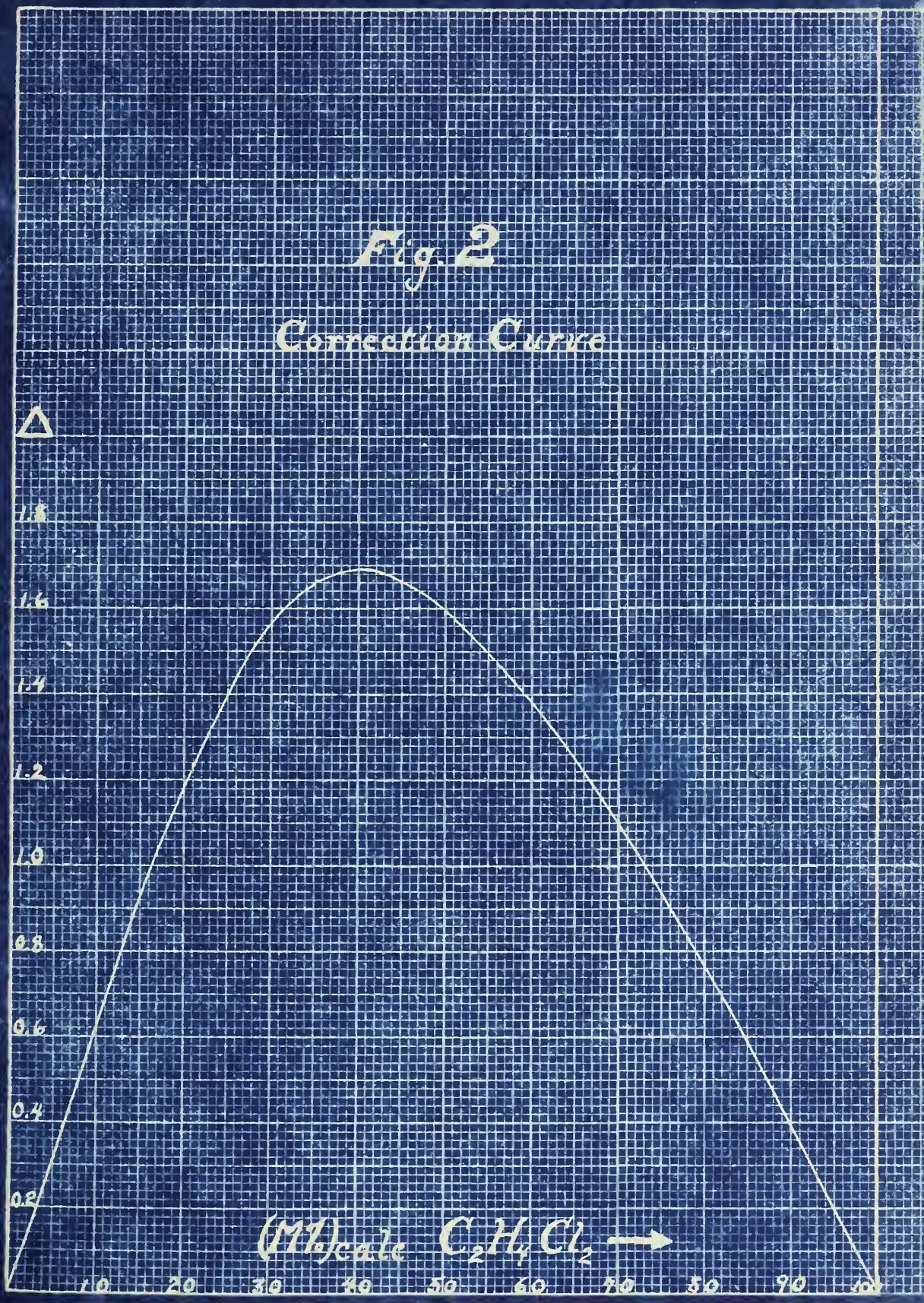
(7) Distil from bright metallic sodium (or Na-K alloy) and preserve over Dehydrite.

Yield, about 65 volume per cent

$n_D^{35.2}$ about 1.4976



Mol percent of C_6H_6 (x)



Mol percent of C_2H_4 (x)

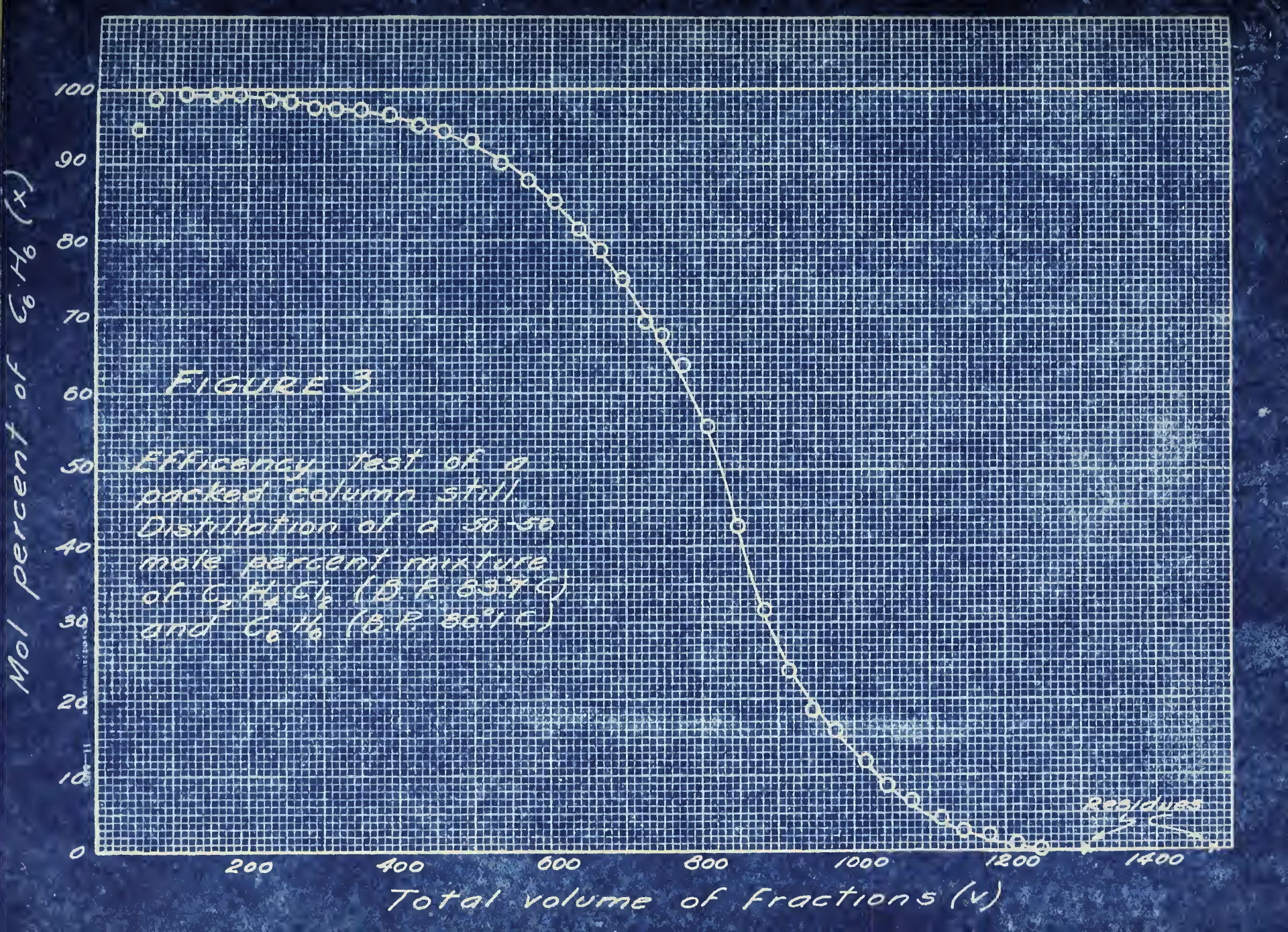


FIGURE 3

Efficiency test of a packed column still. Distillation of a 50-50 mole percent mixture of $C_2H_4Cl_2$ (B.P. 83.7° C) and C_6H_6 (B.P. 80.1° C)

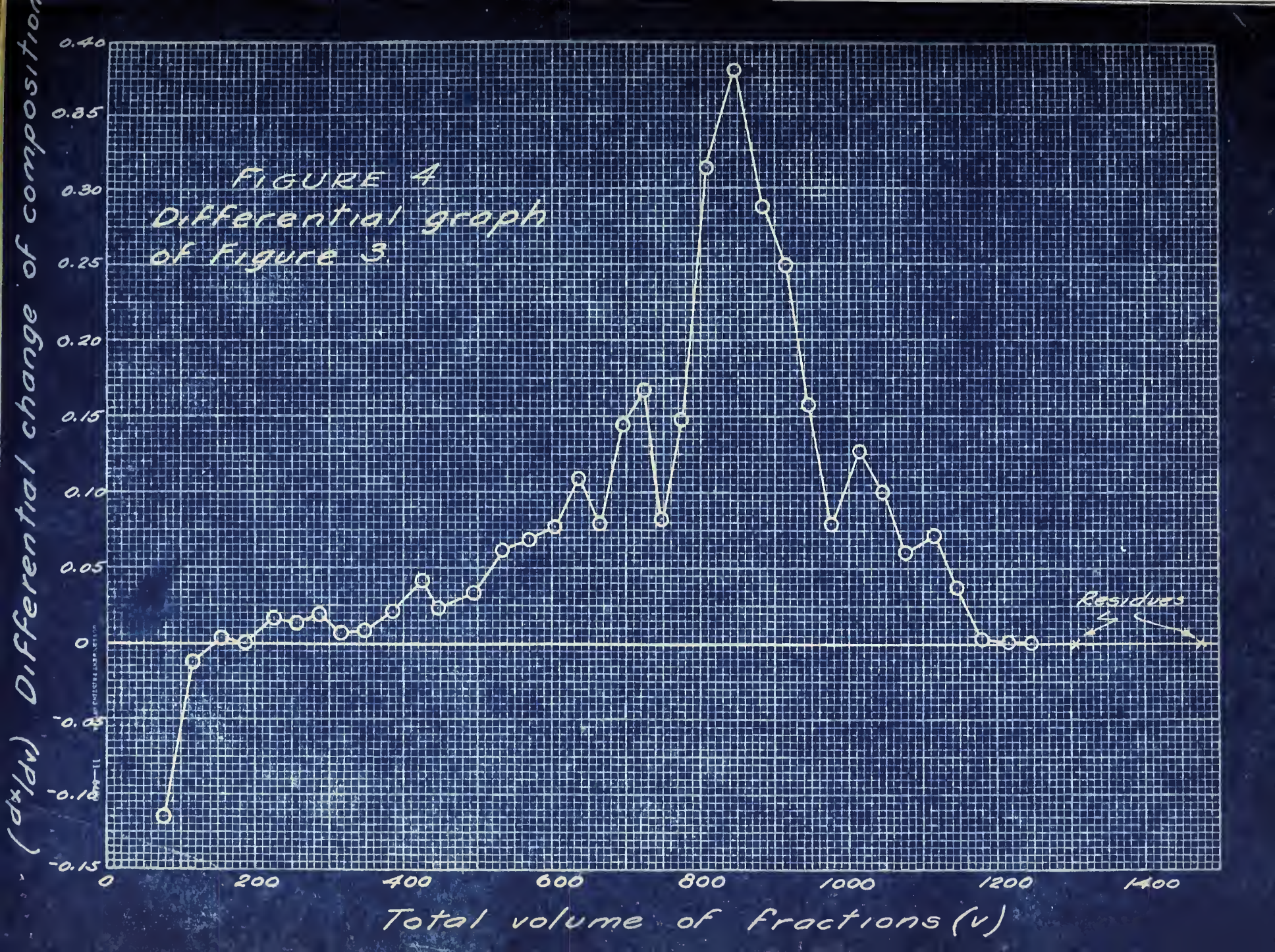


FIGURE 4
Differential graph
of Figure 3
(dx/dv) Differential change of composition
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
-0.05
-0.10
-0.15
0
200
400
600
800
1000
1200
1400
Total volume of fractions (v)
Residues